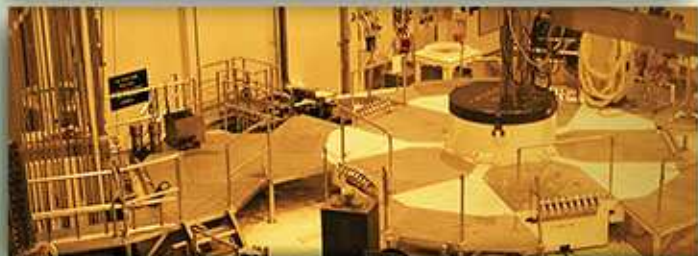
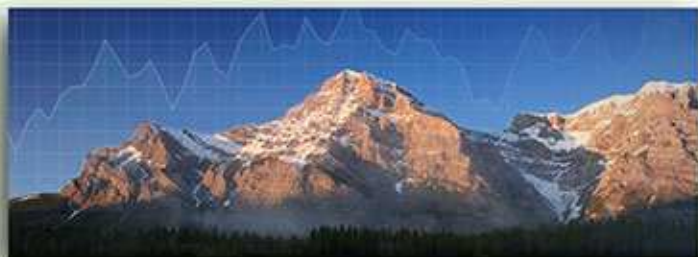


US EPA ARCHIVE DOCUMENT



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## Development of the Integrated Continuous Aerosol Monitoring System (ICAMS)

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**STAR Grants Progress Review Webinar**

April 28, 2010

## Motivation

- Real-time data on reactive nitrogen species are needed at multiple locations to understand fluxes, dynamics of  $\text{PM}_{2.5}$ , and to constrain atmospheric models, etc.
- Existing methods (research and commercial) have proven problematic for widespread deployment
  - Time-consuming
  - Expensive
  - Subject to artifacts
- **Objective:** Modify Southeastern Aerosol Research and Characterization (SEARCH) network continuous measurements of  $\text{PM}_{2.5}$ ,  $\text{NO}_3^-$  &  $\text{NH}_4^+$  and gaseous  $\text{HNO}_3$  and  $\text{NH}_3$  for deployment in State and Local networks.

# Catalytic-Denuder Difference Approach

## Advantages

- Uses commercial chemiluminescence analyzers
- Analyzers are a well-known technology
- Time-tested denuder techniques
- No messy liquids or chemicals

## Disadvantages

- Indirect technique: measures oxidized and reduced forms of nitrogen, not specific compounds

If  $\text{NO}_2$  removed by a KCl denuder, will be interpreted as  $\text{HNO}_3$

- Differencing technique:
  - Noisy when background  $\text{NO}_x$  highly variable (single detector)
  - Noisy when background  $\text{NO}_x$  is high (“needle in haystack”)

## Example: NH<sub>3</sub> Method

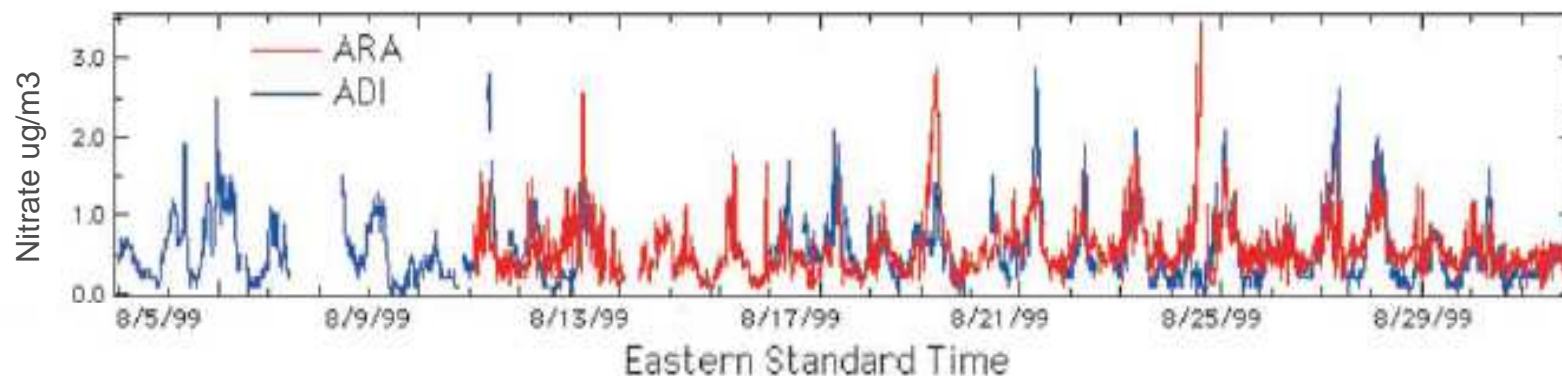
### Two channel oxidized AND reduced nitrogen (TN) analyzer

- Channel 1 samples ambient air through a sodium carbonate denuder then Pt/Mo converters in series (=TN)
- Channel 2 samples ambient air through dual sodium carbonate and citric acid denuders then Pt/Mo converters in series (TN\*)
- NH<sub>3</sub> operationally defined as TN-TN\*

# ICAMS Development Overview: 1999-2009

Supersite Predecessor (1999)	SEARCH and ARA-ICAMS	AQD-ICAMS: Prototype 1
<p><b>NO<sub>3</sub><sup>-</sup></b> Described in Weber 2003 Dual sodium hypochlorite-coated annular denuders to suppress NOx background</p> <p><b>NH<sub>4</sub><sup>+</sup></b> Described in Edgerton 2006 and Solomon &amp; Sioutas 2008 Used a Pt/Alumina catalyst for oxid.</p> <p><b>HNO<sub>3</sub></b> Described in Solomon 2003 2 channel NOy and NOy-HNO<sub>3</sub> difference with KCl denuder Also NOy</p> <p><b>NH<sub>3</sub></b> Not measured</p>	<p><b>NO<sub>3</sub><sup>-</sup></b> Described in Edgerton 2006; Solomon &amp; Sioutas 2008 2 activated carbon honeycomb denuders (MAST 'monolith') to suppress NOx background</p> <p><b>NH<sub>4</sub><sup>+</sup></b> Described in Edgerton et al. 2006; Solomon &amp; Sioutas 2008 2 activated carbon honeycomb denuders (MAST 'monolith') to suppress NOx background Pt/Alumina in shot form for NH<sub>4</sub><sup>+</sup> oxidation (cheaper, conversion at low T, maintains high conversion efficiency longer)</p> <p><b>HNO<sub>3</sub></b> Unchanged</p> <p><b>NH<sub>3</sub></b> Citric acid denuder (sodium carbonate for HNO<sub>3</sub>) Described in Saylor (to be submitted) and Edgerton 2008 AWMA Visibility Meeting</p> <p><b>Other</b> Ballasts to synchronize flows</p> <p>All annular denuders (all but carbon) were URG (SEARCH version) or Sunset (ARA-ICAMS)</p>	<p><b>NO<sub>3</sub><sup>-</sup></b> Zero calculation in software</p> <p><b>NH<sub>4</sub><sup>+</sup></b> Zero calculation in software</p> <p><b>HNO<sub>3</sub></b> Unchanged</p> <p><b>NH<sub>3</sub></b> Tested no sodium carbonate denuder</p> <p><b>Other</b> Robust &amp; compact packaging (1/2 to 2/3 less inlet volume) Ethernet controlled Plumbed for easy maintenance Reduced # ovens Post-process sample averaging</p>

## ICAMS Predecessor: Atlanta Supersite Experiment (1999)

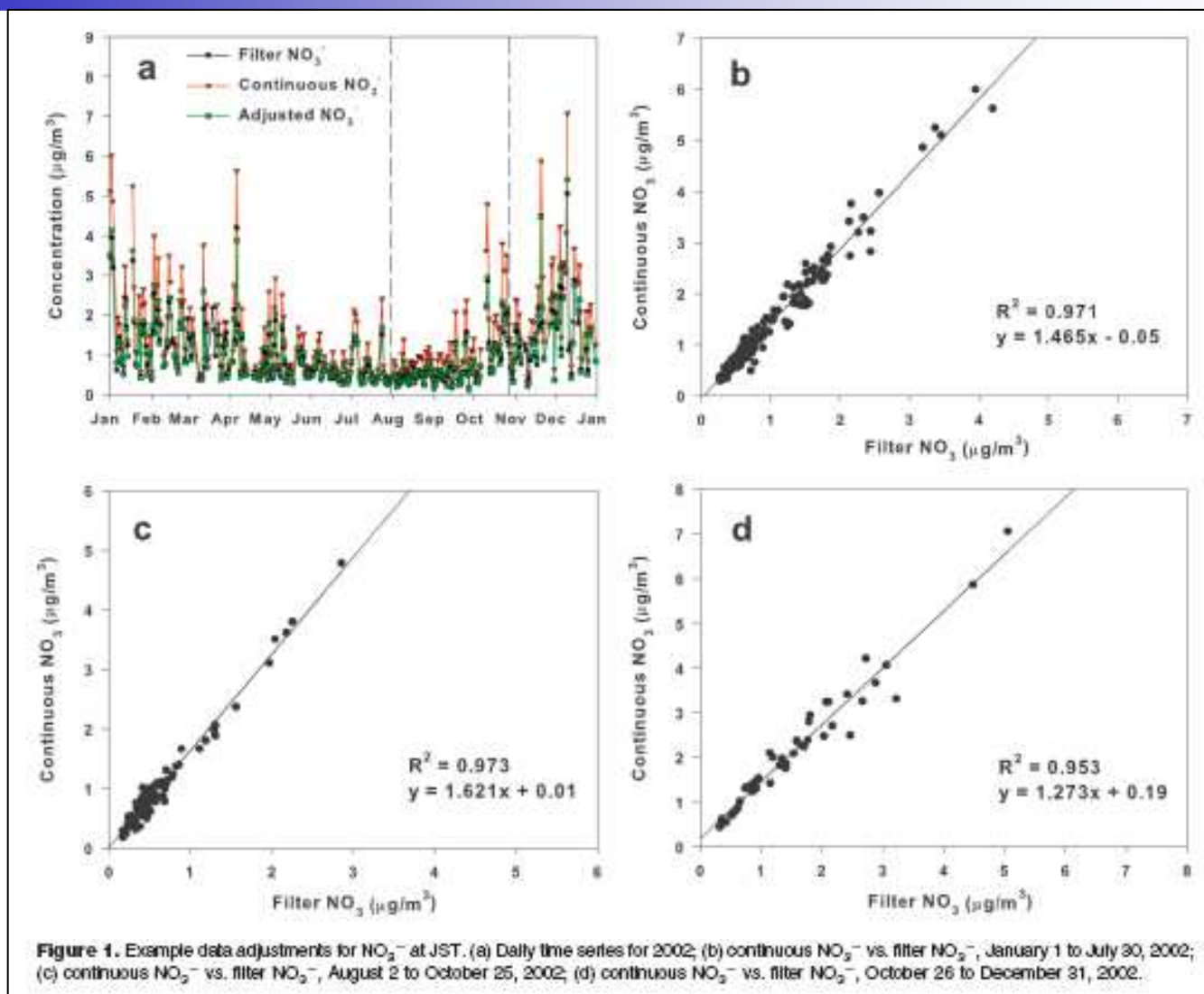


- **Captured time resolution and magnitude similarly to other available instruments**  
(e.g., integrated collection and vaporization cell; Aerosol Dynamics, Inc.; Stolzenburg & Hering (2000))
- **Some differencing errors at low nitrate concentrations; subsequent versions were substantially improved through NO<sub>x</sub> suppression**

*Weber et al. 2003 10.1029/2001JD001220*

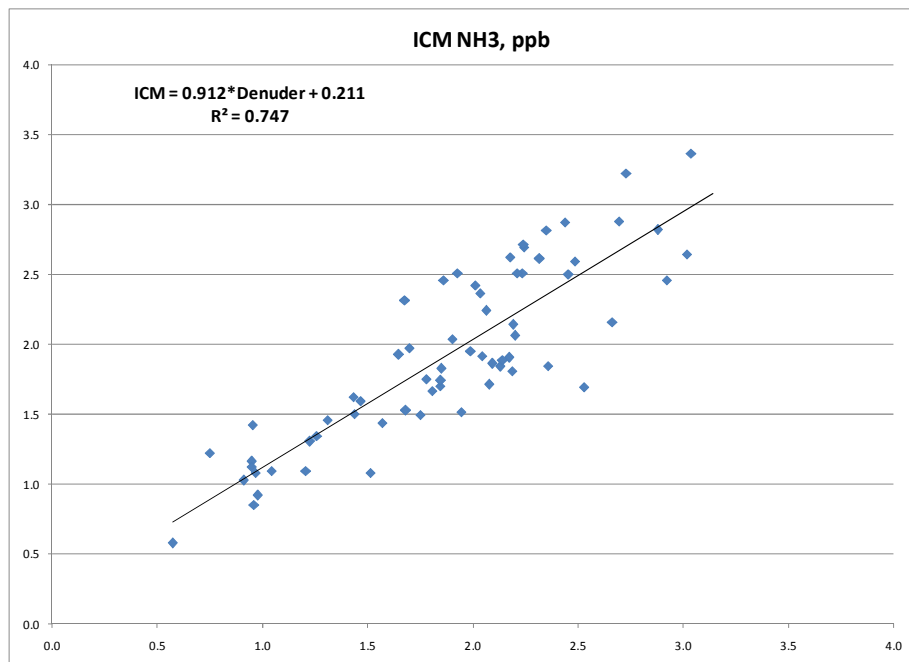


# Further Development: SEARCH Continuous Measurements (2000-2006)

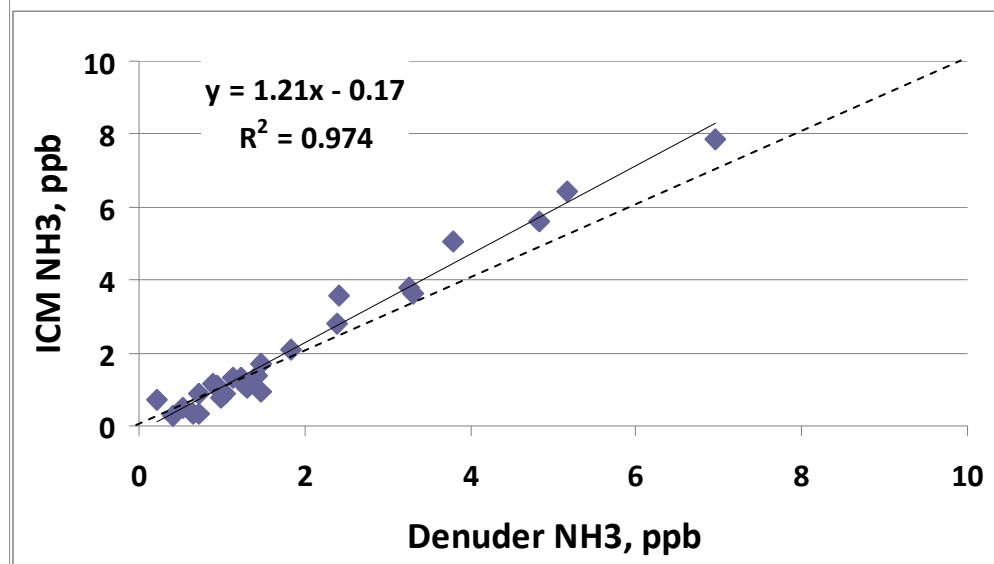




## Example: ARA ICAMS vs. Denuder NH<sub>3</sub>



**JST: Significant scatter; -10% bias**



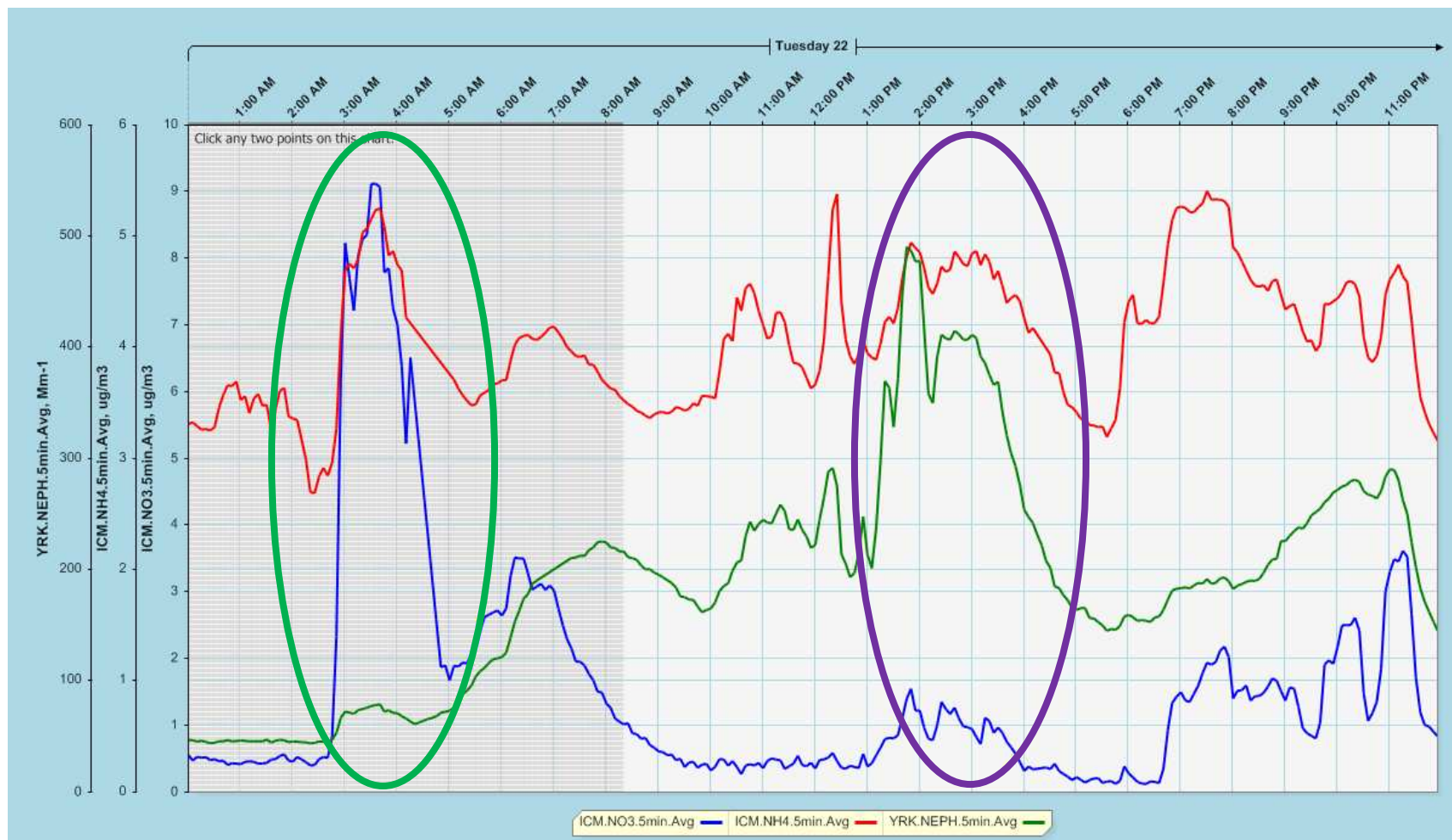
**YRK: Minimal scatter; +20% bias**

## 2007 Field Test Summary

Var.	Site	Det. Lt. <sup>a</sup>	Slope	Int. <sup>a</sup>	r <sup>2</sup>	Prec. (%)
HNO <sub>3</sub>	JST	85	1.01	68	0.93	15
	YRK	36	0.82	105	0.88	18
NH <sub>3</sub>	JST	107	0.91	211	0.75	22
	YRK	48	1.21	-170	0.97	14
NH <sub>4</sub> <sup>+</sup>	JST	99	0.86	404	0.92	8
	YRK	45	1.06	3	0.95	9
NO <sub>3</sub> <sup>-</sup>	JST	58	1.03	-48	0.96	11
	YRK	58	0.96	59	0.98	12

a – units for gases are ppt, units for particles are ng/m<sup>3</sup>

# Short-Term Variability: Two different event types in same day



Early peak (green ellipse) exhibits  $d\text{NH}_4^+/d\text{NO}_3^-$  of 0.31 versus 0.29 for pure  $\text{NH}_4\text{NO}_3$ ; Late peak (purple ellipse) shows only minor increases in  $\text{NO}_3^-$  and  $\text{NH}_4^+$  during major smoke event ( $B_{sp} > 400 \text{ Mm}^{-1}$ ).

## 2007-2008 ARA-ICAMS Status

System	Short description	Conversion/Processing summary	Species reported
1	NO <sub>y</sub> / NO <sub>y</sub> *	350 °C Mo converters; KCl denuder on one channel	NO <sub>y</sub> , HNO <sub>3</sub>
2	TN / TN*	750 °C Pt converters, followed by 350 °C Mo converters. Citric acid denuder on one channel.	NH <sub>3</sub>
3	NH <sub>4</sub> / NO <sub>3</sub>	Gaseous species denuder train followed by combination of 750 °C Pt and 350 °C Mo converters	Particulate NH <sub>4</sub> and NO <sub>3</sub>

- Good agreement (<+/- 25%) with filter/denuder measurements
- 5-minute and 1-hour data show very interesting (and encouraging) short-term behavior
- Prior versions developed by ARA in place at 8 SEARCH network sites.



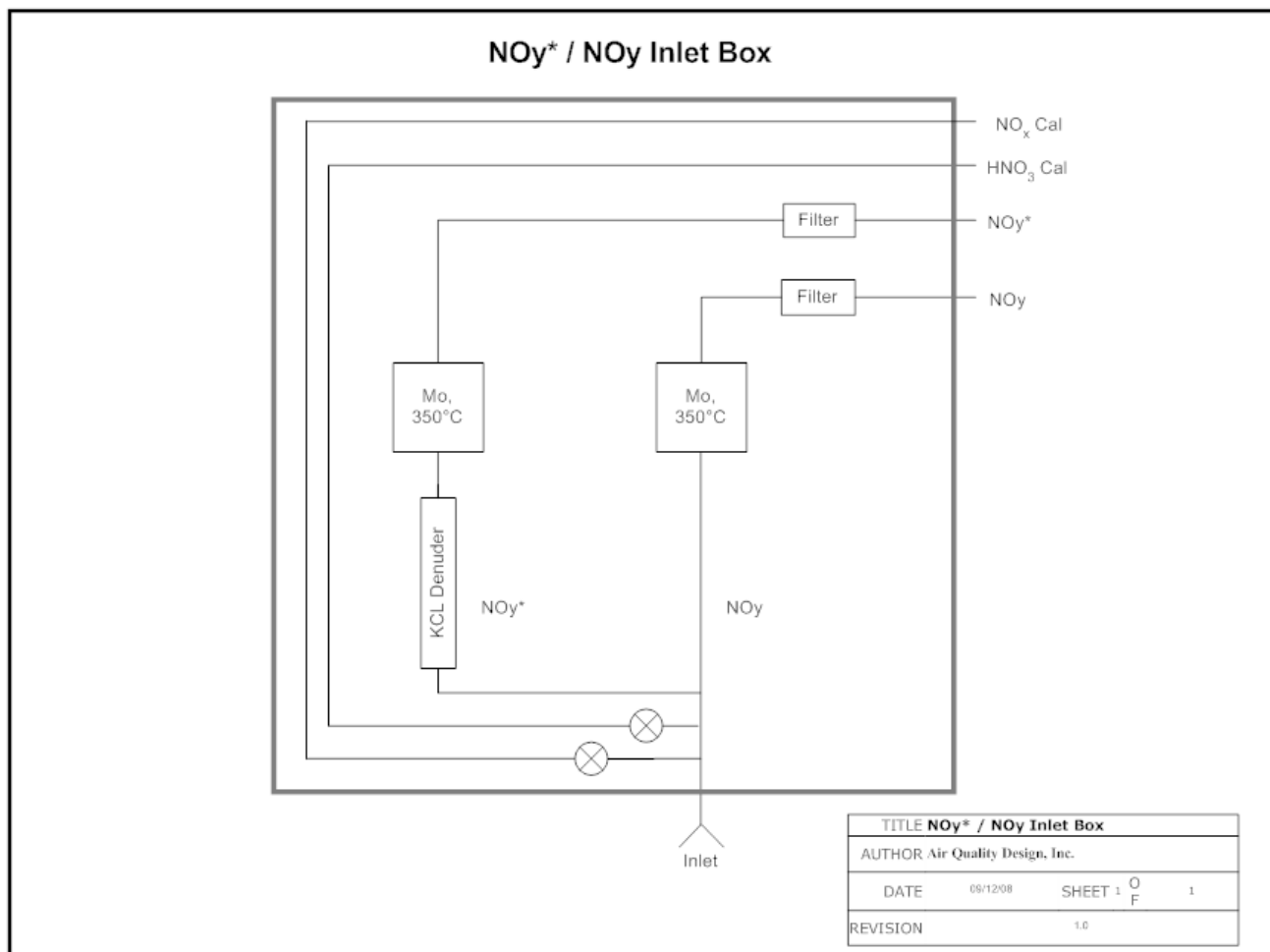
# 2008 Air Quality Design Modifications

**Development Objective: Create a commercial-grade ICAMS that is autonomous, robust, and easy to use.**

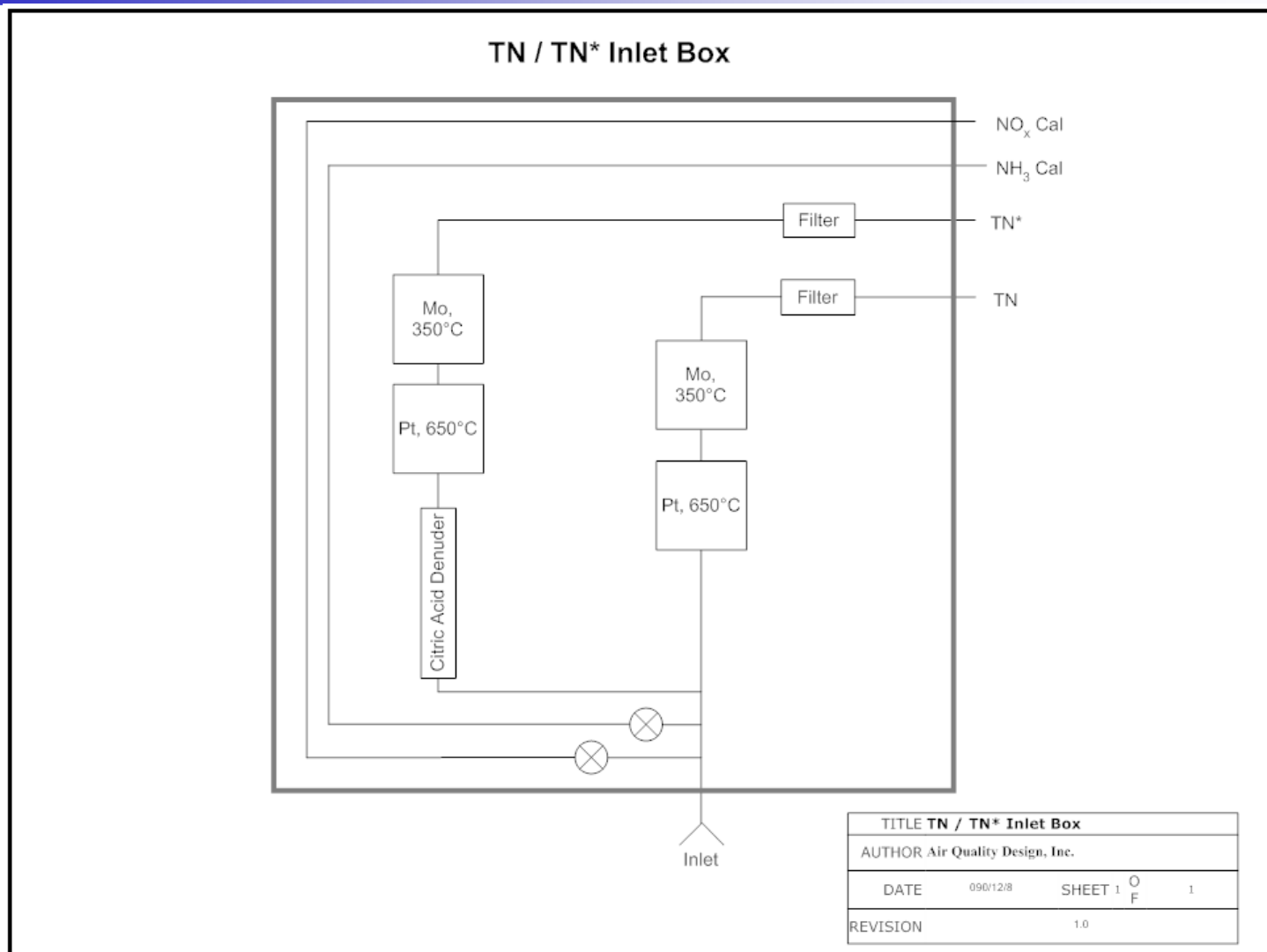
## **Simplify equipment**

- Minimize size & weight of inlet and control systems
- Standardize electrical & pneumatic connectors
- Designed/built double-channel ovens to minimize temperature controlled zones
- Plumbing simplifications
- Ethernet-connected inlet control
- Lightweight, weather-tight, fiberglass enclosures
- Replace 2-L buffer volumes with faster data collection (physical to electronic integration)

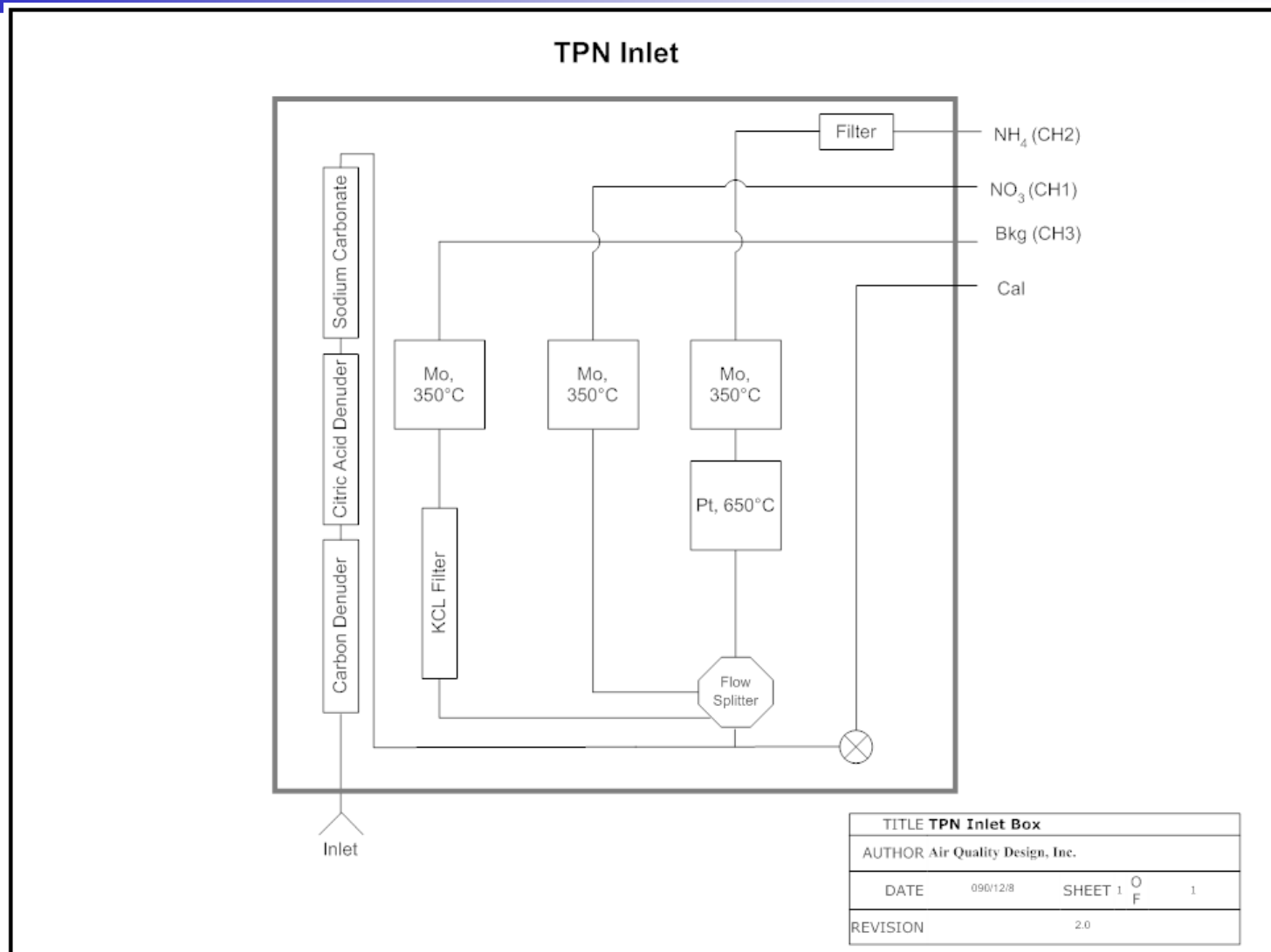
⇒ Net system size reduction of factor of three







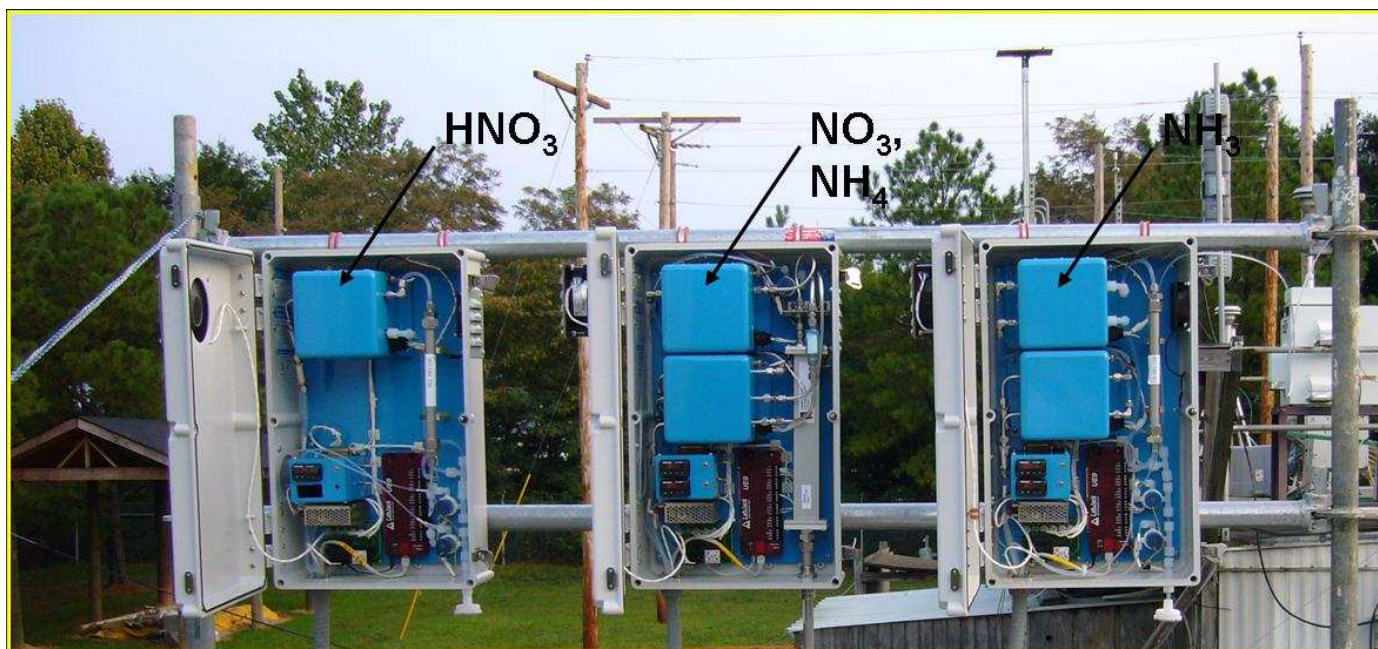
# Particle $\text{NH}_4^+$ & $\text{NO}_3^-$



# 2008 Field Tests: AMIGAS Campaign

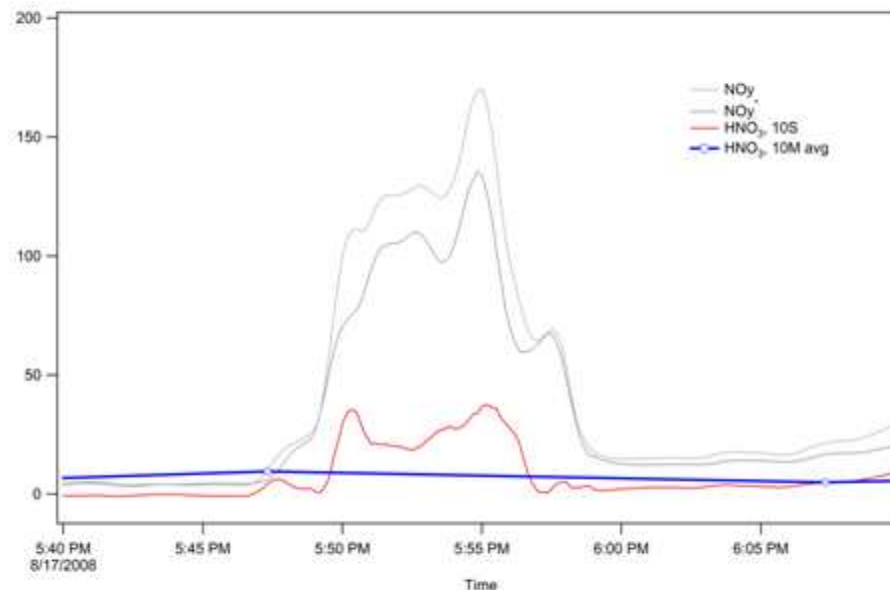
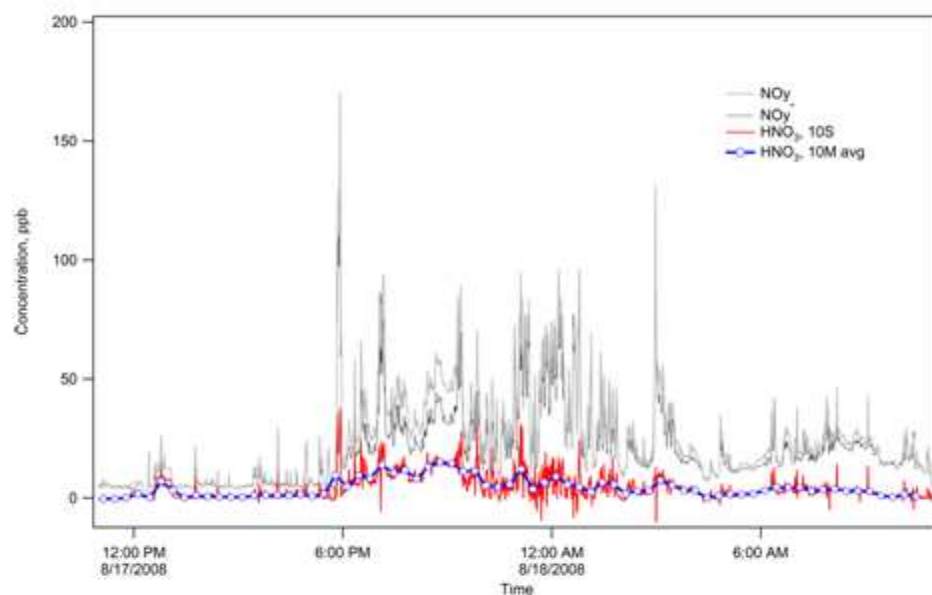
Deployed in August Mini-Intensive Gas and Aerosol Study  
(Atlanta SEARCH) August 2008

- Continuous  $\text{HNO}_3$ ,  $\text{NH}_3$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{NO}_y$  (ARA ICAMS)
- 24-hour filter  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ; Continuous  $\text{NO}$ ,  $\text{NO}_2$ ; 24-hour  $\text{NH}_3$  (ARA)
- PILS-IC  $\text{NO}_3^-$ ,  $\text{NH}_4^+$  (Weber)



# HNO<sub>3</sub> Results

- Very good performance. No loss of denuder efficiency over two weeks.
- Rapid time response and measurement precision were realized.

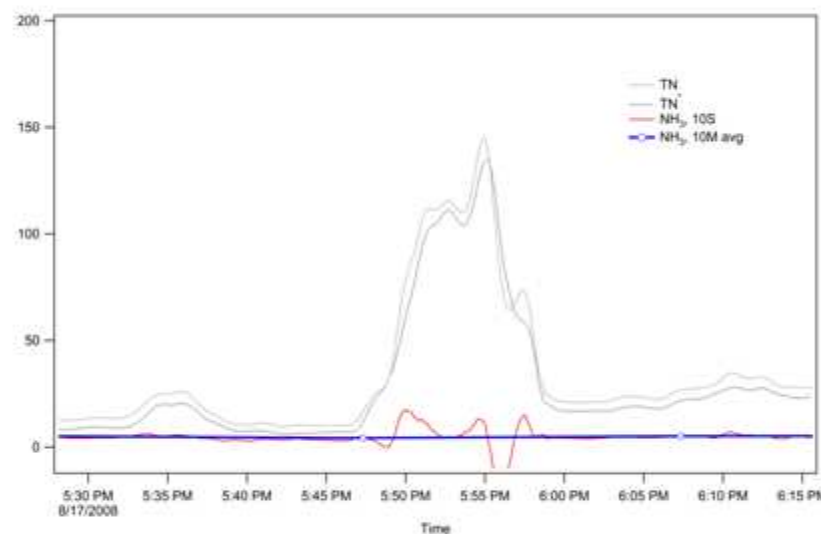
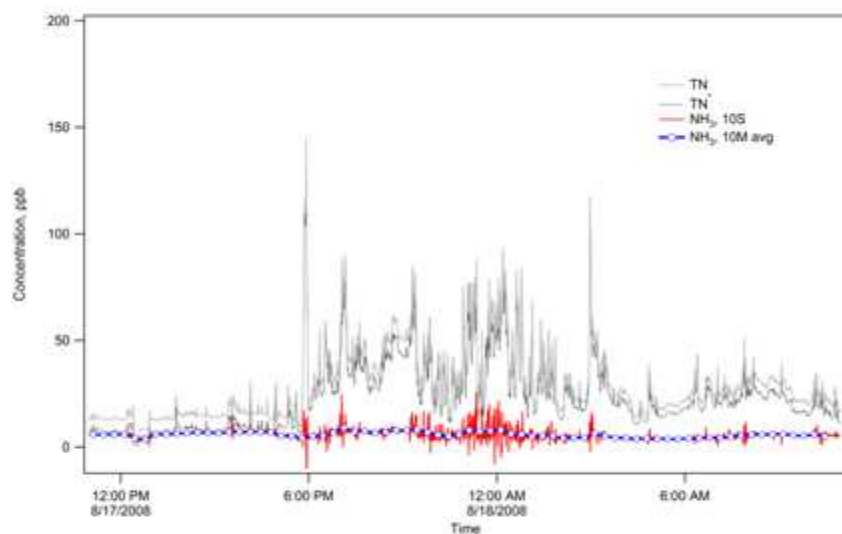


**Left: 24-hour time series for NO<sub>y</sub>, NO<sub>y</sub>\* and HNO<sub>3</sub>.**

**Right: view of the peak observed at about 6 P.M. on 8/17/08.**

# NH<sub>3</sub> Results

- Very good performance. No loss of denuder efficiency over two weeks.
- Rapid time response and measurement precision were realized.
- Transients results from different time response between channels, but no meaningful change in the NH<sub>3</sub> concentration

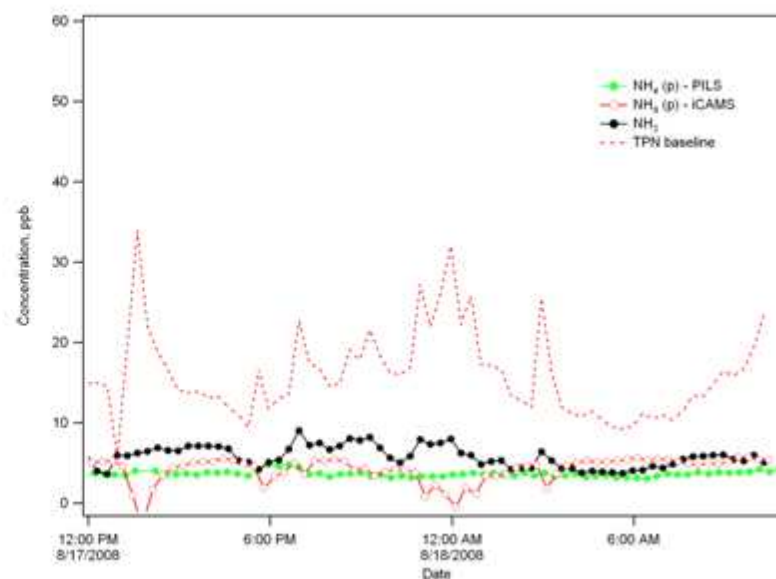
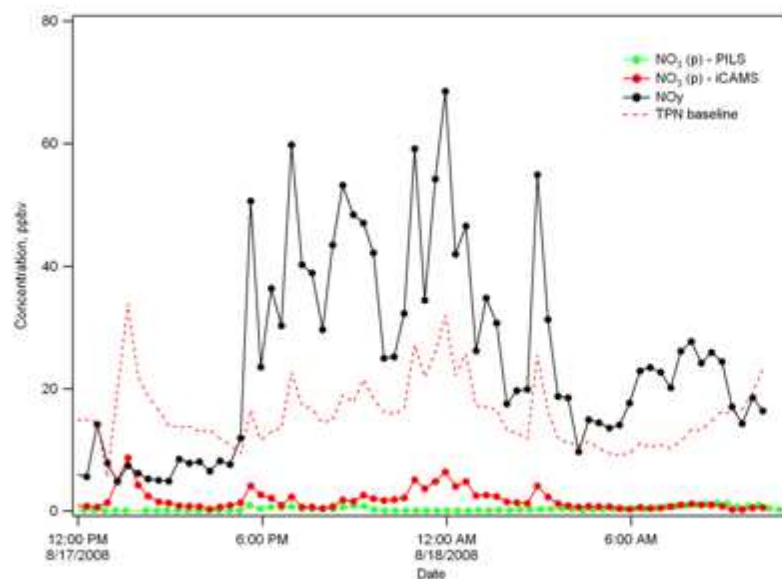


**Left: 24-hour time series for TN, TN\* and NH<sub>3</sub>.**

**Right: view of the peak observed at about 6 P.M. on 8/17/08**

# Particle Results

- Clearly influenced by background NO<sub>x</sub> & NO<sub>y</sub>.
- Specific denuder used for NO<sub>x</sub> suppression didn't work. Expect MAST activated carbon honeycomb used previously should provide comparable performance.



**Left: Nitrate channel, TPN baseline, and ambient NO<sub>y</sub> signal.**

**Right: Ammonium channel, TPN baseline and ambient ammonia signal.**

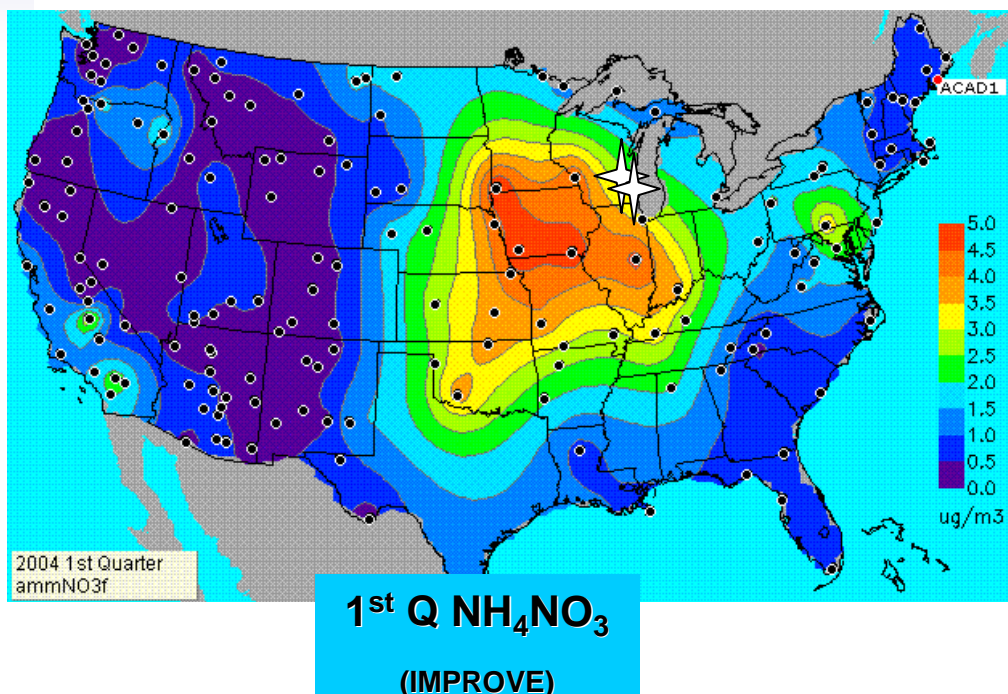


# First AQD Commercial Prototype

- AQD ICAMS is a streamlined, and weather-proof version suitable for research applications where the user is willing to perform maintenance of changing all denuders every few weeks.
- AQD is currently ready to offer an ICAMS inlet system paired with available commercial NO monitors in a three-instrument form.
- The total estimated cost of the system is \$99,000.
  - NOx instruments constitutes about \$40,000.
  - Inlet \$22,000
  - Modifications & packaging \$30,000
  - Other \$7,000



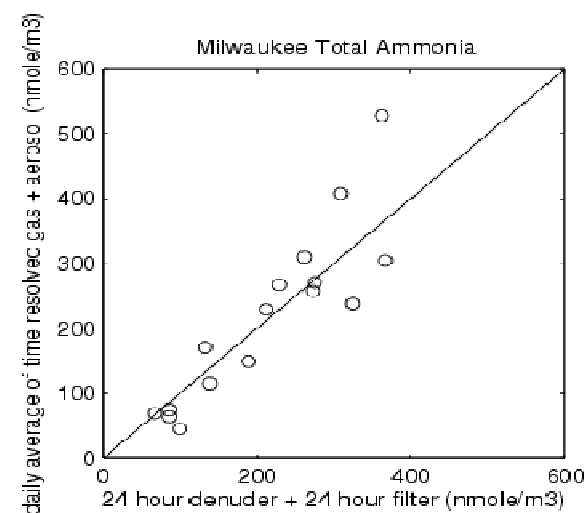
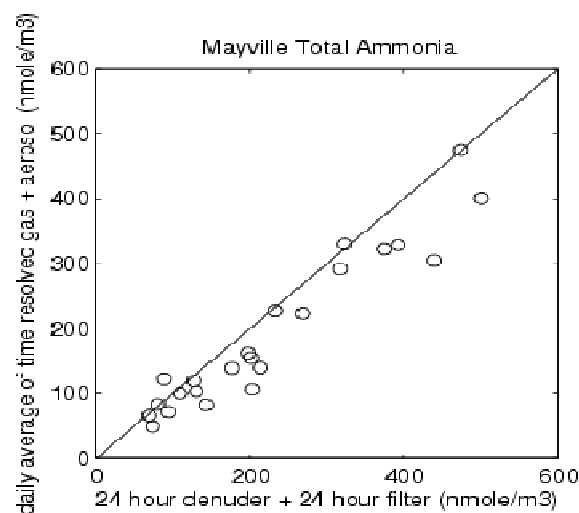
# 2008-2009 Winter Nitrate Study



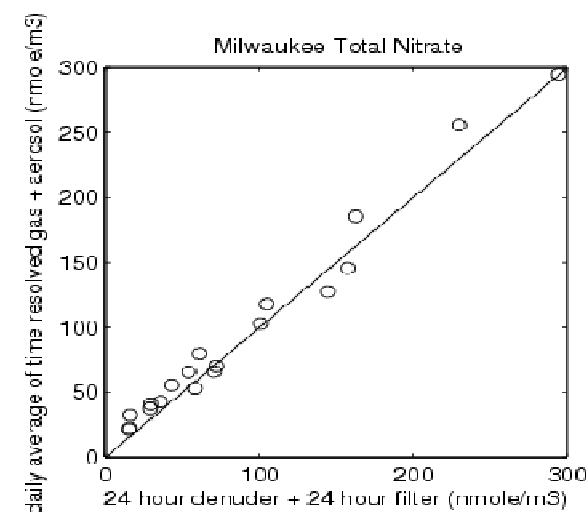
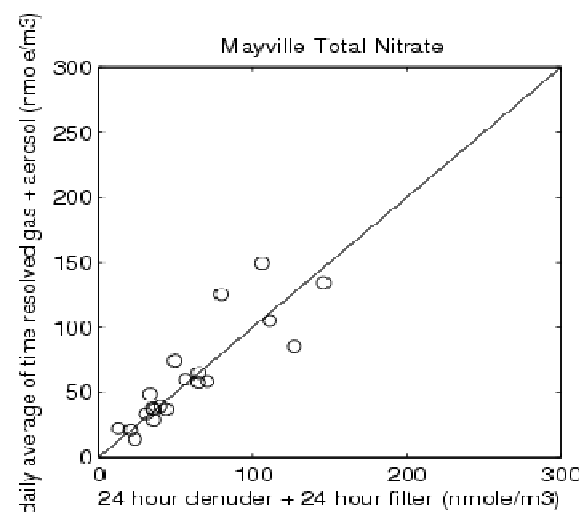
- LADCO-sponsored field campaign
- Urban-rural at Mayville and Milwaukee, WI
- WI DNR provided analyzers, sites, operators; ARA provided ICAMS measurements
- Real-time  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{HNO}_3$ ,  $\text{NH}_3$
- Data analysis by U. Iowa & U. Illinois
- Plus suite of WI network data
- Complementary SEARCH data will be used to evaluate chemical mechanisms

# Continuous vs. 24hr Data: Total Ammonia & Nitrate

**Total  
Ammonia**  
→  
**NH<sub>3</sub> + NH<sub>4</sub><sup>+</sup>**



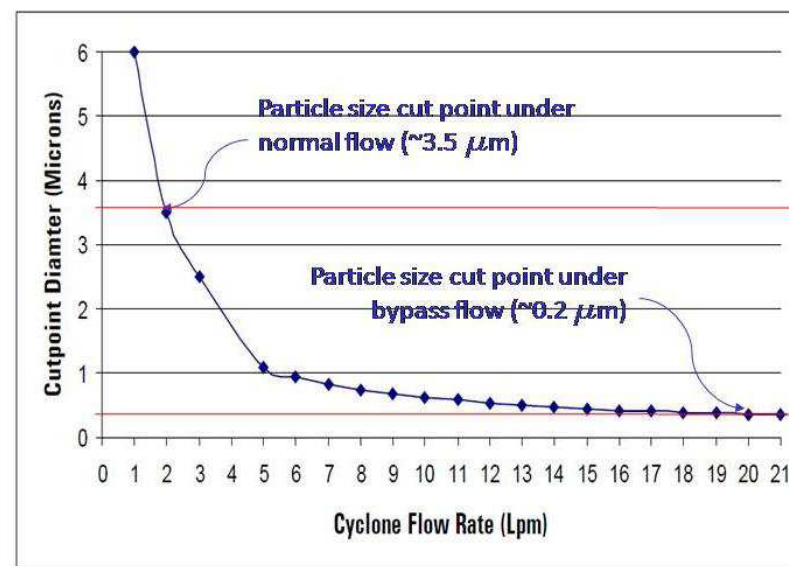
**Total Nitrate**  
→  
**HNO<sub>3</sub> + NO<sub>3</sub><sup>-</sup>**



# 2009 Development Plans

## AQD developed alternate approach to maintaining low NO<sub>x</sub> baseline

- Assume converters used for HNO<sub>3</sub> and NH<sub>3</sub> are also suitable for NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>. Validated in ambient measurements for NO<sub>3</sub><sup>-</sup> (e.g. Fahey, et al, 1989).
- Inertial particle separation method
  - Two-mode cyclone operation: 2 slpm for whole air and 20 slpm for gases only
  - Inert surface important for quantitative transfer of HNO<sub>3</sub> and NH<sub>3</sub>
  - Alternate to selective filtering and gas elimination in prior design
- By-product is simplification
  - Mechanical: 2 instruments, not 3!
  - Philosophy: direct measure of gas background for particle signal



# November 2009 Inlet Design



Mo oven  
Pt oven

Temp controllers  
Ethernet DAQ device  
Citric Acid denuder  
Bypass pump  
Flow splitter  
T-controlled cyclone



## 2009 Field Results



Jefferson Street in Atlanta, GA  
12/15/09 through 2/26/10

- Calibrations stable; reactive gas denuders maintained their efficiency over two-month deployment.
- Ambient T  $\sim 6^{\circ}\text{C}$ , so low-temperature inlet intended to eliminate  $\text{NH}_4\text{NO}_3$  volatilization occasionally froze.
- Large change in flowrate increased reactive gas transmission through the cyclone and possibly surface desorption. Made gas channel higher than gas+particle channel, so particle numbers not quantifiable.
- Frequency of ambient  $\text{NO}_y$  and TRN variability was often faster than 3-min cycle so gases not quantifiable. Do not want physical sample integration (ballast) for network - will modify plumbing.



# Future Development

Measurements not yet as robust as original design, but just begun

## Compared to other approaches:

(e.g. filter-based measurements or steam-extraction/ion chromatography)

- Require regular attendance by qualified technicians
- Considerable consumable reagents and materials

## Potential ICAMS benefits:

- Higher data frequency
- Autonomous operation
- Agencies familiar with detectors
- Reduction in the number of instruments to be deployed
- Reduced cost

## Next:

- Return to earlier, more complex versions?
- AQD awarded SBIR funds for continued focus on the two instrument system

## Relevant Publications (1/2)

- Solomon, P.; Sioutas, C., Continuous and semicontinuous monitoring techniques for particulate matter mass and chemical components: A synthesis of findings from EPA's particulate matter supersites program and related studies. *Journal of the Air & Waste Management Association* **2008**, 58, (2), 164-195.
- Edgerton, E. S.; Saylor, R. D.; Hartsell, B. E.; Jansen, J. J.; Hansen, D. A., Ammonia and ammonium measurements from the southeastern United States. *Atmospheric Environment* **2007**, 41, (16), 3339-3351.
- Edgerton, E. S.; Hartsell, B. E.; Saylor, R. D.; Jansen, J. J.; Hansen, D. A.; Hidy, G. M., The Southeastern Aerosol Research and Characterization Study, Part 3. Continuous measurements of fine particulate matter mass and composition. *Journal of the Air & Waste Management Association* **2006**, 56, (9), 1325-1341.
- Edgerton, E. S.; Hartsell, B. E.; Saylor, R. D.; Jansen, J. J.; Hansen, D. A.; Hidy, G. M., The southeastern aerosol research and characterization study: Part 2. Filter-based measurements of fine and coarse particulate matter mass and composition. *Journal of the Air & Waste Management Association* **2005**, 55, (10), 1527-1542.

## Relevant Publications (2/2)

- Hansen, D. A.; Edgerton, E. S.; Hartsell, B. E.; Jansen, J. J.; Kandasamy, N.; Hidy, G. M.; Blanchard, C. L., The southeastern aerosol research and characterization study: Part 1. Overview. *Journal of the Air & Waste Management Association* **2003**, 53, (12), 1460-1471.
- Solomon, P.; Baumann, K.; Edgerton, E.; Tanner, R.; Eatough, D.; Modey, W.; Marin, H.; Savoie, D.; Natarajan, S.; Meyer, M. B.; Norris, G., Comparison of integrated samplers for mass and composition during the 1999 Atlanta Supersites project. *Journal of Geophysical Research-Atmospheres* **2003**, 108, (D7).
- Weber, R.; Orsini, D.; Duan, Y.; Baumann, K.; Kiang, C. S.; Chameides, W.; Lee, Y. N.; Brechtel, F.; Klotz, P.; Jongejan, P.; ten Brink, H.; Slanina, J.; Boring, C. B.; Genfa, Z.; Dasgupta, P.; Hering, S.; Stolzenburg, M.; Dutcher, D. D.; Edgerton, E.; Hartsell, B.; Solomon, P.; Tanner, R., Intercomparison of near real time monitors of PM<sub>2.5</sub> nitrate and sulfate at the US Environmental Protection Agency Atlanta Supersite. *Journal of Geophysical Research-Atmospheres* **2003**, 108, (D7).
- Fehsenfeld, F.; Huey, L.; Leibrock, E.; Dissly, R.; Williams, E.; Ryerson, T.; Norton, R.; Sueper, D.; Hartsell, B., Results from an informal intercomparison of ammonia measurement techniques. *Journal of Geophysical Research-Atmospheres* **2002**, 107, (D24).

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